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(54) Title: POWDER COATING COMPOSITIONS FOR THE PRODUCTION OF LOW-GLOSS COATINGS

(57) Abstract

Disclosed are powder coating compositions comprised of one or more semi-crystalline polyesters, one or more hydroxyl acrylic polymers and a blocked polyisocyanate cross-linking agent. Coatings of the compositions on shaped metal articles exhibit an ASTM D-523-85 60° gloss value of not greater than 35, ASTM D-2794-84 front/back impact strength values of at least 40/20 inch-pounds and an ASTM D-3359-83 cross-hatch adhesion pass percent value of at least 90.

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POWDER COATING COMPOSITIONS FOR THE PRODUCTION OF LOW-GLOSS COATINGS

This invention pertains to certain novel, thermosetting powder coating compositions which produce low-gloss (matte) coatings on various substrates. More particularly, this invention pertains to powder coating compositions comprising a novel combination of one or more semi-crystalline, hydroxyl polyesters and one or more hydroxyl acrylic polymers.

Thermosetting powder coating compositions are used extensively to produce durable protective coatings on various materials. Thermosetting coatings, when compared to coatings derived from thermoplastic compositions, generally are tougher, more resistant to solvents and detergents, have better adhesion to metal substrates, and do not soften when exposed to elevated temperatures. Thermosetting powder coating compositions possess certain significant advantages over solvent-based coating compositions which are inherently undesirable because of the environmental and safety problems occasioned by the evaporation of the solvent system. Solvent-based coating compositions also suffer from the disadvantage of relatively poor percent utilization, i.e., in some modes of application, only 60 percent or less of the solvent-based coating composition being applied contacts the article or substrate being coated. Thus, a substantial portion of solvent-based coatings can be wasted since that portion which does not contact the article or substrate being coated obviously cannot be reclaimed.

Coatings derived from thermosetting coating compositions should exhibit or possess good impact strength, hardness, flexibility, and resistance to

solvents and chemicals. It is essential that powder coating compositions remain in a free-flowing, finely divided state for a reasonable period after they are manufactured and packaged. Thus, polyesters utilized in powder coating formulations desirably possess a glass transition temperature (Tg) higher than the storage temperatures to which the formulations will be exposed. Semi-crystalline polyesters and blends thereof with amorphous polyesters also may be utilized in powder coating formulations. For this application, semi-crystalline polyesters desirably possess a significant degree of crystallinity to prevent caking or sintering of the powder for a reasonable period of time prior to its application to a substrate. Semi-crystalline polyesters used in powder coating formulations also must have melting temperature low enough to permit the compounding of the powder coating formulation without causing the cross-linking agent to react prematurely with the polyesters. The lower melting temperature of the semi-crystalline polyester also is important to achieving good flow of the coating prior to curing and thus aids the production of smooth and glossy coatings.

Finally, the production of tough coatings which are resistant to solvents and chemicals requires adequate cross-linking of the powder coating compositions at curing temperatures and times commonly employed in the industry. In the curing of powder coating compositions, a coated article typically is heated at a temperature in the range of about 325 to 400°F (163-204°C) for up to about 20 minutes causing the coating particles to melt and flow followed by reaction of the cross-linking (curing) agent with the polyester. The degree of curing

may be determined by the methyl ethyl ketone rub test described hereinbelow. Normally, a thermosetting coating is considered to be completely or adequately cross-linked if the coating is capable of sustaining 200 double rubs. It is apparent that the use of lower temperatures and/or shorter curing times to produce adequately cross-linked coatings is very advantageous since higher production rates and/or lower energy costs can be achieved thereby.

For certain end uses such as office furniture, automotive exterior trim and automotive after market parts, a coating having low gloss is desired. Known methods for preparing powder coating compositions which produce low-gloss coatings include blending two or more finished powder coating compositions or by blending fillers or extenders with a coating composition. These methods are time consuming and/or can result in powder coating compositions which produce coatings deficient in one or more of the properties refereed to hereinabove.

We have discovered that coatings having low gloss and good to excellent hardness, impact strength (toughness), flexibility, and resistance to solvents and chemicals may be obtained by the use of powder coating compositions comprising a combination of a semi-crystalline polyester, a hydroxyl acrylic polymer and a blocked polyisocyanate compound. The powder coating compositions provided by this invention thus comprise an intimate blend, typically in a finely divided form, of:

(1) a blend of polymers consisting essentially of:

(A) 30 to 70 weight percent, based on the weight of the blend of polymers, of a semi-crystalline polyester having a glass transition temperature (Tg) of less than 50°C,

a hydroxyl number of about 20 to 100, an inherent viscosity of about 0.1 to 0.5, a melting range of about 70 to 150°C, a number average molecular weight of about 1500 to 10,000, and a heat of fusion (second heating cycle of DSC) of greater than about 5 cal/g-°C, e.g. 5 to about 20 cal/g-°C; and

(B) 70 to 30 weight percent of a hydroxyl acrylic polymer having a glass transition temperature (Tg) of greater than 40°C and a hydroxyl number of about 20 to 100; and

(2) a cross-linking effective amount of a blocked polyisocyanate compound.

The powder coating compositions encompassed by our invention are further characterized by producing coatings, e.g. from about 1 to 4 mils thick, on metals which exhibit an ASTM D-523-85 60° gloss value of not greater than 35, ASTM D2794-84 front/back impact strength values of at least 40/20 inch-pounds and an ASTM D-3359-83 cross-hatch adhesion pass percent value of at least 90.

Examples of the semi-crystalline polyesters which may be used in the manufacture of the powder coating compositions are set forth in U.S. Patent 4,859,760. Suitable semi-crystalline polyesters meeting the criteria set forth hereinabove include polyesters comprised of (1) a diacid component comprised of at least 50, preferably at least 90 mole percent terephthalic or 1,4-cyclohexanedicarboxylic acid residues and (2) diol residues comprised of about 0 to 20 mole percent 2,2-dimethyl-1,3-propanediol residues and about 80 to 100 mole percent of residues of one or more diols having the formula $-O-(CH_2)_n-O-$ wherein n is

4 to about 12. The semi-crystalline polyester preferably is comprised of (1) diacid residues comprised of (a) about 80 to 98 mole percent terephthalic acid residues and (b) about 2 to 20 mole percent of 1,4-cyclohexanedicarboxylic acid residues, 1,3-cyclohexanedicarboxylic acid residues, adipic acid residues or a mixture thereof, and (2) diol residues comprised of at least about 50 mole percent of residues having the formula $-O-(CH_2)_n-O-$ wherein n is 4 to about 12.

The semi-crystalline polyester component, in addition to the residues specified hereinabove, may contain minor amounts, e.g., up to 10 mole percent based upon the total monomer residues of the polyester, of other diacid and diol residues such as the residues of ethylene glycol, propylene glycol, 1,3-propanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-2-isobutyl-1,3-propanediol, 1,3-butanediol, thiodiethanol, 1,2-, 1,3- and 1,4-cyclohexanedimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 1,4-xylylenediol and residues of succinic, glutaric, adipic, azelaic, sebacic, fumaric, maleic, itaconic, phthalic and/or isophthalic acids. The 1,3- and 1,4-cyclohexane-dicarboxylic acid or the dialkyl esters thereof used in the preparation of the polyesters may be the trans isomer, the cis isomer, or a mixture of such isomers. Preferably, the cis:trans ratio is in the range of about 30:70 to about 70:30.

The semi-crystalline polyester preferably has a Tg of less than about 30°C, e.g., about 0 to 30°C, a hydroxyl number of about 30 to 80, an inherent viscosity of about 0.1 to 0.5, a melting range of about 90 to 140°C, and a number average molecular weight of about 2000 to 6000. The heat of fusion (second heating cycle

of DSC) of the preferred semi-crystalline polyesters is greater than about 8 cal/g-°C, e.g., from about 8 to 15 cal/g-°C. Semi-crystalline polyesters are those that exhibit an endothermic transition on a differential scanning calorimetry (DSC) scan from low to high temperature. Such a transition also is referred to as melting, a destruction of the orderly arranged molecular structure. The preferred semi-crystalline polyesters comprise (1) diacid residues consisting essentially of about 85 to 95 mole percent terephthalic acid residues and about 5 to 15 mole percent 1,3-cyclohexane-dicarboxylic or 1,4-cyclohexanedicarboxylic acid residues, preferably having a trans isomer content of about 35 to 65 mole percent and (2) diol residues consisting essentially of residues having the formula $-O-(CH_2)_n-O-$ wherein n is 6 to 12, especially 1,6-hexanediol.

The hydroxyl acrylic polymers useful in the preparation of our novel compositions have a glass transition temperature (Tg) of greater than 40°C and a hydroxyl number of about 20 to 100. Examples of suitable hydroxyl acrylic polymers are sold under the names SCJ-800B, SCJ-802 and Joncryl 587 by S. C. Johnson. These acrylic polymers may be prepared by known solution polymerization processes.

The hydroxyl acrylic polymer utilized in the powder coating composition of this invention typically contains about 80-95 weight percent methyl methacrylate or styrene or a mixture of methyl methacrylate, styrene, and 5-20 weight percent of a hydroxyalkyl methacrylate or a hydroxyalkyl acrylate each having 2-4 carbon atoms in the alkyl groups or mixtures thereof. Optionally, up to 10 weight percent of an alkyl methacrylate or an

alkyl acrylate having 2-14 carbon atoms in the alkyl groups and may be present in the acrylic polymer to provide a polymer having a glass transition temperature within the range specified above. A minor amount of acrylic acid also may be present to enhance the adhesion of the hydroxyl acrylic polymer.

Examples of such hydroxyl acrylic polymers include polymers composed of 82-94 weight percent methyl methacrylate, 1-10 weight percent of the alkyl acrylate or methacrylate, 5-17% by weight of the hydroxy alkyl acrylate or methacrylate, e.g., an acrylic polymer consisting of methyl methacrylate, lauryl methacrylate, hydroxyethyl acrylate, or hydroxypropyl methacrylate or consisting of methyl methacrylate and hydroxy propyl methacrylate.

Typical alkyl acrylates and alkyl methacrylates having 2-14 carbon atoms in the alkyl groups that can be used to prepare the acrylic polymer are as follows: ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, nonyl acrylate, decyl acrylate, lauryl acrylate, tetradecyl acrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, decyl methacrylate, lauryl methacrylate, tetradecyl methacrylate and the like.

Typical hydroxyalkyl acrylates and methacrylates which can be used to prepare the acrylic polymer are 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, and the like. Hydroxyethyl acrylate and hydroxypropyl methacrylate are preferred. Hydroxypropyl methacrylate

is a mixture of 2-hydroxypropyl methacrylate and 1-methyl-2-hydroxyethyl methacrylate. One particularly useful mixture is of 68-75% of 2-hydroxy propyl methacrylate and 1-methyl-2-hydroxyethyl methacrylate.

The blend of polymers, i.e., component (1), present in the powder coatings of this invention consists essentially of, in general, 30 to 70 weight percent semi-crystalline, hydroxyl polyester and 70 to 30 weight percent hydroxyl acrylic polymer, based on the weight of the polymer blend. Thus, the compositions do not contain a significant amount, e.g., not greater then about 5 weight percent, of other curable or cross-linkable polymers which materially changes the properties of the coatings obtained from the coating compositions. However, the relative amounts of specific polyesters and acrylic polymers may vary within the above-specified ranges so that the powder coating composition produces on shaped metal objects coatings which exhibit an ASTM D-523-85 60° gloss value of not greater than 35, an ASTM D2794-84 front/back impact strength values of at least 40/20 inch-pounds and an ASTM 3358-83 cross-hatch adhesion pass percent value of at least 90. The powder coating compositions of this invention preferably produce on shaped metal objects coatings having an ASTM D-523-85 60° gloss value of not greater than 20 and contain a polymer blend consisting essentially of about 40 to 60 weight percent of the semi-crystalline polyester and about 60 to 40 weight percent of the hydroxyl acrylic polymer.

The blocked polyisocyanate cross-linking component of the powder coating compositions of this invention are known compounds and can be obtained from commercial sources or may be prepared according to published

procedures. Upon being heated to cure coatings of the compositions, the compounds are unblocked and the isocyanate groups react with hydroxy groups present on the semi-crystalline polyester and the acrylic polymer to cross-link the polymer chains and thus cure the compositions to form tough coatings. Examples of the blocked polyisocyanate cross-linking component include those which are based on isophorone diisocyanate blocked with ε-caprolactam, commercially available as Hüls B1530, Ruco NI-2 and Cargill 2400, or toluene 2,4-diisocyanate blocked with ε-caprolactam, commercially available as Cargill 2450, and phenol-blocked hexamethylene diisocyanate.

The most readily-available, and thus the preferred, blocked polyisocyanate cross-linking agents or compounds are those commonly referred to as ε-caprolactam-blocked isophorone diisocyanate, e.g., those described in U.S. Patents 3,822,240, 4,150,211 and 4,212,962. However, the products marketed as ε-caprolactam-blocked isophorone diisocyanate may consist primarily of the blocked, difunctional, monomeric isophorone diisocyanate, i.e., a mixture of the cis and trans isomers of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, the blocked, difunctional dimer thereof, the blocked, trifunctional trimer thereof or a mixture of the monomeric, dimeric and/or trimeric forms. For example, the blocked polyisocyanate compound used as the cross-linking agent may be a mixture consisting primarily of the ε-caprolactam-blocked, difunctional, monomeric isophorone diisocyanate and the ε-caprolactam-blocked, trifunctional trimer of isophorone diisocyanate. The description herein of the cross-linking agents as "polyisocyanates" refers to compounds

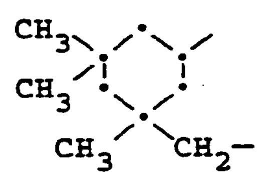
which contain at least two isocyanato groups which are blocked with, i.e., reacted with, another compound, e.g., ε-caprolactam. The reaction of the isocyanato groups with the blocking compound is reversible at elevated temperatures, e.g., about 150°C and above, at which temperature the isocyanato groups are available to react with the hydroxyl groups present on the semi-crystalline polyester and acrylic polymer to form urethane linkages.

Another class of blocked polyisocyanate compounds which may be employed as the cross-linking agent of the powder coating compositions are adducts of the 1,3-diazetidine-2,4-dione dimer of isophorone diisocyanate and a diol, wherein the adducts have the structure

$$OCN{-}R^1\left[X{-}R^1{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}R^2{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R^1\right]_n X{-}R^1{-}NCO$$

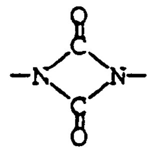
wherein

R^1 is a divalent 1-methylene-1,3,3-trimethyl-5-cyclohexyl radical, i.e., a radical having the structure



R^2 is a divalent aliphatic, cycloaliphatic, araliphatic or aromatic residue of a diol; and

X is a 1,3-diazetidine-2,4-dionediyl radical, i.e., a radical having the structure



wherein the ratio of NCO to OH groups in the formation of the adduct is about 1:0.5 to 1:0.9, the mole ratio of diazetidinedione to diol is from 2:1 to 6:5, the content of free isocyanate groups in the adduct is not greater than 8 weight percent and the adduct has a molecular weight of about 500 to 4000 and a melting point of about 70 to 130°C.

The above-described adducts may be prepared according to the procedures described in U.S. Patent 4,413,079 by reacting the diazetidine dimer of isophorone diisocyanate, preferably free of isocyanurate trimers of isophorone diisocyanate, with diols in a ratio of reactants which gives as isocyanto:hydroxyl ratio of about 1:0.5 to 1:0.9, preferably 1:0.6 to 1:0.8. The adduct preferably has a molecular weight of 1450 to 2800 and a melting point of about 85 to 120°C. The preferred diol reactant is 1,4-butanediol. Such an adduct is commercially available under the name Hüls BF1540.

The amount of the blocked polyisocyanate cross-linking compound present in the compositions of our invention can be varied depending on several factors such as the properties and characteristics of the particular semi-crystalline polyester and/or hydroxyl acrylic polymer employed, the particular cross-linking agent used, the degree of pigment loading, the properties required of the coatings to be prepared from the compositions, etc. Typically, the amount of cross-linking compound which will effectively cross-link the

hydroxy-containing polymers to produce coatings having a good combination of properties is in the range of about 5 to 30 weight percent, preferably 15 to 25 weight percent, based on the total weight of the semi-crystalline polyester, the acrylic polymer and the cross-linking compound.

The powder coating compositions of our invention may be prepared from the compositions described herein by dry-mixing and then melt-blending the semi-crystalline polyester, the hydroxyl acrylic polymer and the blocked polyisocyanate compound, along with other additives commonly used in powder coatings, and then grinding the solidified blend to a particle size, e.g., an average particle size in the range of about 10 to 300 microns, suitable for producing powder coatings. For example, the ingredients of the powder coating composition may be dry blended and then melt blended in a Brabender extruder at 90 to 130°C, granulated and finally ground. The melt blending should be carried out at a temperature sufficiently low to prevent the unblocking of the polyisocyanate cross-linking compound and thus avoid premature cross-linking. To minimize the exposure of the blocked polyisocyanate to elevated temperatures, the semi-crystalline polyesters and acrylic polymers may be blended prior to the incorporation therein of the blocked polyisocyanate compound.

Typical of the additives which may be present in the powder coating compositions include benzoin, used to reduce entrapped air or volatiles, flow aids or flow control agents which aid the formation of a smooth surface, catalysts to promote the cross-linking reaction between the isocyanate groups of the cross-

linking agent and the hydroxyl groups on the polymers, stabilizers, pigments and dyes. Although it is possible to cure or cross-link the composition without the use of a catalyst, it is usually desirable to employ a catalyst to aid the cross-linking reaction, e.g., in an amount of about 0.05 to 2.0 weight percent cross-linking catalyst based on the total weight of the semi-crystalline hydroxyl polyester, the hydroxyl acrylic polymer and the cross-linking agent. Suitable catalysts for promoting the cross-linking include organo-tin compounds such as dibutyltin dilaurate, dibutyltin dimaleate, dibutyltin oxide, stannous octanoate and similar compounds.

The powder coating compositions preferably contain a flow aid, also referred to as flow control or leveling agents, to enhance the surface appearance of cured coatings of the powder coating compositions. Such flow aids typically comprise acrylic polymers and are available from several suppliers, e.g., Modaflow from Monsanto Company and Acronal from BASF. Other flow control agents which may be used include Modarez MFP available from Synthron, EX 486 available from Troy Chemical, BYK 360P available from BYK Mallinkrodt and Perenol F-30-P available from Henkel. A specific flow aid is an acrylic polymer having a molecular weight of about 17,000 and containing 60 mole percent 2-ethylhexyl methacrylate residues and about 40 mole percent ethyl acrylate residues. The amount of flow aid present may be in the range of about 0.5 to 4.0 weight percent, based on the total weight of the semi-crystalline polyester, the acylic polymer and the cross-linking agent.

The powder coating compositions may be deposited on various metallic and non-metallic substrates by known

techniques for powder deposition such as by means of a powder gun, by electrostatic deposition or by deposition from a fluidized bed. In fluidized bed sintering, a preheated article is immersed into a suspension of the powder coating in air. The particle size of the powder coating composition normally is in the range of 60 to 300 microns. The powder is maintained in suspension by passing air through a porous bottom of the fluidized bed chamber. The articles to be coated are preheated to about 250 to 400°F (about 121 to 205°C) and then brought into contact with the fluidized bed of the powder coating composition. The contact time depends on the thickness of the coating that is to be produced and typically is from 1 to 12 seconds. The temperature of the substrate being coated causes the powder to flow and thus fuse together to form a smooth, uniform, continuous, uncratered coating. The temperature of the preheated article also affects cross-linking of the coating composition and results in the formation of a tough coating having a good combination of properties. Coatings having a thickness between 200 and 500 microns may be produced by this method.

The compositions also may be applied using an electrostatic process wherein a powder coating composition having a particle size of less than 100 microns, preferably about 15 to 50 microns, is blown by means of compressed air into an applicator in which it is charged with a voltage of 30 to 100 kV by high-voltage direct current. The charged particles then are sprayed onto the grounded article to be coated to which the particles adhere due to the electrical charge thereof. The coated article is heated to melt and cure

the powder particles. Coating of 40 to 120 microns thickness may be obtained.

Another method of applying the powder coating compositions is the electrostatic fluidized bed process which is a combination of the two methods described above. For example, annular or partially annular electrodes are mounted over a fluidized bed so as to produce an electrostatic charge such as 50 to 100 kV. The article to be coated, either heated, e.g., 250 to 400°F, or cold, is exposed briefly to the fluidized powder. The coated article then can be heated to effect cross-linking if the article was not preheated to a temperature sufficiently high to cure the coating upon contact of the coating particles with the article.

The powder coating compositions of this invention may be used to coat articles of various shapes and sizes constructed of heat-resistant materials such as glass, ceramic and various metal materials. The compositions are especially useful for producing coatings on articles constructed of metals and metal alloys, particularly steel articles.

The compositions and coatings of our invention are further illustrated by the following examples. The inherent viscosities (I.V.; dl/g) referred to herein were measured at 25°C using 0.5 g polymer per 100 mL of a solvent consisting of 60 parts by weight phenol and 40 parts by weight tetrachloroethane. Melt viscosities (poise) were determined using an ICI melt viscometer according to ASTM D4287-83. Acid and hydroxyl numbers were determined by titration and are reported herein as mg of KOH consumed for each gram of polymer. The glass transition temperatures (Tg) and the melting temperatures (Tm) were determined by differential

scanning calorimetry (DSC) on the second heating cycle at a scanning rate of 20°C per minute after the sample was heated to melt and quenched to below the Tg of the polymer. Tg values are reported as the midpoint of the transition and Tm at peaks of transitions. The weight average molecular weight (Mw) and number average molecular weight (Mn) were determined by gel permeation chromatography in tetrahydrofuran (THF) using a polystyrene standard and a UV detector.

Coatings were prepared on 3 inch by 9 inch panels of 24-gauge, polished, cold roll steel, the surface of which has been zinc phosphated (Bonderite 37, The Parker Company). Impact strengths were determined using an impact tester (Gardner Laboratory, Inc.) according to ASTM D2794-84. A weight with a 5/8-inch diameter, hemispherical nose was dropped within a slide tube from a specified height to drive into the front (coated face) or back of the panel. The highest impact which did not crack the coating was recorded in inch-pounds, front and reverse. The 20° and 60° gloss values were measured using a glossmeter according to ASTM D-523-85. The adhesion values (% pass) were determined according to ASTM D-3359-83.

The pencil hardness of the coatings was determined according to ASTM 3363-74 (reapproved 1980) and is reported as the hardest lead which does not cut into the coating. The reults of the pencil hardness test are expressed according to the following scale: (softest) 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H (hardest). The conical mandrel test is conducted according to ASTM 522-85 by bending a panel over a 15 second period using a conical mandrel (Gardner

Laboratory, Inc.) of a specified size. A pass or fail is recorded.

The following reference examples describe the preparation of semi-crystalline, hydroxyl polyesters suitable for use in the manufacture of the powder coating compositions.

REFERENCE EXAMPLE 1

To a 5-L, 3-neck, round-bottom flask are charged terephthalic acid (1300.6 g, 7.83 mol), neopentyl glycol (132.1 g, 1.27 mol), 1,6-hexanediol (849.1 g, 7.19 mol) and dibutyltin oxide (2.3 g). The flask is purged with nitrogen and heated to 190°C over approximately 1.5 hours. The batch is maintained at 190°C until 15-20% of theoretical condensate has evolved at which time the batch temperature is increased to and maintained at 230°C until the acid number is at or below 10 mg KOH/g polymer. The molten polymer is poured into a syrup can where it cools to a white solid. The polyester thus obtained had an I.V. of 0.310, an ICI melt viscosity at 200°C of 19.0 poise, a hydroxyl number of 50 and an acid number of 5. Differential scanning calorimetry (second cycle) showed a melting point at 126°C, a crystallization temperature of 43°C, a Tg of 10°C, a heat of crystallization of -6.5 cal/g and a heat of fusion of 10.9 cal/g. The polyester had a weight average molecular weight of 14,800 and a number average molecular weight of 3800 (Mw/Mn = 3.89).

REFERENCE EXAMPLE 2

Terephthalic acid (2092.8 g, 12.60 mol), 1,4-cyclohexanedicarboxylic acid (cis:trans = about 60:40, 114.2 g, 0.66 mol), and butanestannoic acid (FASCAT 4100, 3.5 g) wer added to a melt of 1,6-hexanediol (1797 g, 15.20 mol) in a 5 L, 3-necked, round-bottom flask. The

contents of the flask were swept with 1.0 standard cubic feet per hour (scfh) nitrogen and heated to 200°C over a period of about 30 minutes. The reaction mixture was heated at 200°C for 3 hours, at 210°C for 2 hours and at 220°C for 1 hour. The temperature then was raised to and maintained at 230°C until the acid number of the polyester was less than 10. The molten polymer was poured into a syrup can where it was allowed to cool to a white solid. The polyester thus obtained had an I.V. of 0.224, an ICI melt viscosity at 200°C of 3.3 poise, a hydroxyl number of 42.5 and an acid number of 2.3. Differential scanning calorimetry showed a melting point at 135°C and a heat of fusion of 10.9 cal/g. No temperature of crystallization was observed. The crystallization half time from the melt at 95°C was 11 seconds and at 60°C was too fast to observe. The polyester had a weight average molecular weight of 9027 and a number average molecular weight of 3666 (Mw/Mn = 2.5).

REFERENCE EXAMPLE 3

Terephthalic acid (519.6 g, 3.127 mol) and butanestannoic acid (FASCAT 4100, 0.8 g) were added to a melt of 1,6-hexanediol (370.9 g, 3.139 mol) and trimethylolpropane (22.2 g, 0.165 mol) in a 1 L, 3-necked, round-bottom flask. The contents of the flask were swept with 1.0 standard cubic feet per hour (scfh) nitrogen and heated to 200°C over a period of about 30 minutes. The reaction mixture was heated at 200°C for 3 hours, at 210°C for 2 hours and at 220°C for 1 hour. The temperature then was raised to and maintained at 230°C until the acid number of the polyester was less than 10. The molten polymer was poured into a syrup can where it was allowed to cool to a white solid. The

polyester thus obtained had an I.V. of 0.30, an ICI melt viscosity of 24 poise, a hydroxyl number of 34 and an acid number of 2. Differential scanning calorimetry showed a melting point at 133°C and a heat of fusion of 8.9 cal/g. The polyester had a weight average molecular weight of 17,098 and a number average molecular weight of 5344.

REFERENCE EXAMPLE 4

Terephthalic acid (360.5 g, 2.17 mol), adipic acid (16.69 g, 0.114 mol) and butanestannoic acid (FASCAT 4100, 0.6 g) were added to a melt of 1,6-hexanediol (309.6 g, 2.62 mol) in a 1 L, 3-necked, round-bottom flask. The contents of the flask were swept with 1.0 standard cubic feet per hour (scfh) nitrogen and heated to 200°C over a period of about 30 minutes. The reaction mixture was heated at 200°C for 3 hours, at 210°C for 2 hours and at 220°C for 1 hour. The temperature then was raised to and maintained at 230°C until the acid number of the polyester was less than 10. The molten polymer was poured into a syrup can where it was allowed to cool to a white solid. The polyester thus obtained had an I.V. of 0.191, an ICI melt viscosity at 200°C of 3.8 poise, a hydroxyl number of 51.0 and an acid number of 0.4. Differential scanning calorimetry showed a melting point at 139°C, a crystallization temperature of 39°C and a heat of fusion of 11.8 cal/g. The crystallization half time from the melt at 95°C was 25 seconds and at 60°C, less than 12 seconds. The polyester had a weight average molecular weight of 7679 and a number average molecular weight of 3564.

REFERENCE EXAMPLE 5

Terephthalic acid (253.87 g, 1.523 mol), 1,4-cyclohexanedicarboxylic acid (cis:trans = about 60:40, 48.4 g, 0.27 mol), and butanestannoic acid (FASCAT 4100, 0.6 g) were added to a melt of 1,10-decanediol (369.9 g, 2.13 mol) in a 5 L, 3-necked, round-bottom flask. The contents of the flask were swept with 1.0 standard cubic feet per hour (scfh) nitrogen and heated to 200°C over a period of about 30 minutes. The reaction mixture was heated at 200°C for 3 hours, at 210°C for 2 hours and at 220°C for 1 hour. The temperature then was raised to and maintained at 230°C until the acid number of the polyester was less than 10. The molten polymer was poured into a syrup can where it was allowed to cool to a white solid. The polyester thus obtained had an I.V. of 0.222, an ICI melt viscosity at 200°C of 2.4 poise, a hydroxyl number of 43.0 and an acid number of 0.2. Differential scanning calorimetry showed a melting point at 116°C and a heat of fusion of 15.1 cal/g. No crystallization temperature was observed. The crystallization half time from the melt at 95°C was 45 seconds and at 60°C, less than 12 seconds. The polyester had a weight average molecular weight of 9746 and a number average molecular weight of 4451.

REFERENCE EXAMPLE 6

Terephthalic acid (284.25 g, 1.711 mol), 1,4-cyclohexanedicarboxylic acid (16.0 g, 0.090 mol) and butanestannoic acid (FASCAT 4100, 0.6 g) were added to a melt of 1,10-decanediol (370.6 g, 2.31 mol) in a 1 L, 3-necked, round-bottom flask. The contents of the flask were swept with 1.0 standard cubic feet per hour (scfh) nitrogen and heated to 200°C over a period of

about 30 minutes. The reaction mixture was heated at 200°C for 3 hours, at 210°C for 2 hours and at 220°C for 1 hour. The temperature then was raised to and maintained at 230°C until the acid number of the polyester was less than 10. The molten polymer was poured into a syrup can where it was allowed to cool to a white solid. The polyester thus obtained had an I.V. of 0.236, an ICI melt viscosity at 200°C of 2.4 poise, a hydroxyl number of 42.0 and an acid number of 0.2. Differential scanning calorimetry showed a melting point at 122°C and a heat of fusion of 16.0 cal/g. The crystallization half time from the melt at 95°C was 15 seconds and was too fast to measure at 60°C. The polyester had a weight average molecular weight of 9915 and a number average molecular weight of 4492.

REFERENCE EXAMPLE 7

Terephthalic acid (304.0 g, 1.830 mol) and butanestannoic acid (FASCAT 4100, 0.6 g) were added to a melt of 1,10-decanediol (356.1 g, 2.046 mol) and 2,2-dimethyl-1,3-propanediol (11.2 g, 0.106 mol)in a 1 L, 3-necked, round-bottom flask. The contents of the flask were swept with 1.0 standard cubic feet per hour (scfh) nitrogen and heated to 200°C over a period of about 30 minutes. The reaction mixture was heated at 200°C for 3 hours, at 210°C for 2 hours and at 220°C for 1 hour. The temperature then was raised to and maintained at 230°C until the acid number of the polyester was less than 10. The molten polymer was poured into a syrup can where it was allowed to cool to a white solid. The polyester thus obtained had an I.V. of 0.209, an ICI melt viscosity at 200°C of 2.4 poise, a hydroxyl number of 46 and an acid number of 2. Differential scanning calorimetry showed a melting temperature at 123°C and a

heat of fusion of 16.0 cal/g. The polyester had a weight average molecular weight of 9786 and a number average molecular weight of 4451.

The powder coating compositions described in the following examples were prepared from a semi-crystalline, hydroxyl polyester and a hydroxyl acrylic polymer supplied by S.C. Johnson & Co. One of the acrylic polymers, referred to hereinbelow as SCJ-800B had an ICI melt viscosity of 25 poise, a hydroxyl number of 43 and a Tg of 43°C. Another hydroxyl acrylic polymer employed, referred to herein below as SCJ-587, had a hydroxyl number of 92, a Tg of 45°C and a molecular weight of 5400.

EXAMPLE 1

A powder coating composition was prepared from the following materials:

664.5 g	Polyester of Reference Example 1;
996.8 g	Hydroxyl acrylic polymer SCJ-800B
281.7 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The above materials were mixed in a Henschel high speed mixer for 45 to 60 seconds and compounded in a W&P twin screw, 30 mm extruder. The extruder temperature profile was: zone 1 = 110°C, zone 2 = 100°C. The extrudate was cooled through a chilled roll and ground in a Bantam mill to which a stream of liquid nitrogen was fed and classified through a 170 mesh screen using a Chemutek classifier. The finely-divided, powder coating

composition obtained had an average particle size of about 50 microns.

The powder coating composition prepared in Example 1 was applied electrostatically to one side of the 3 inch by 9 inch panels described hereinabove. The coatings were cured (cross-linked) by heating the coated panels at 375°F (190.5°C) in an oven for 20 minutes. The cured coatings were about 2.0 mils (about 50 microns) thick.

The coatings on the panels had both front and back impact strengths of 160 inch-pounds and 20° and 60° gloss values of 5 and 16, respectively, and a pencil hardness of 3H. The coated panels passed a 0.125 inch conical mandrel test and had a cross-hatch adhesion test value of 95% pass.

EXAMPLE 2

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

1006.5 g	Polyester of Reference Example 1;
670.3 g	Hydroxyl acrylic polymer SCJ-800B
266.2 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had both front and back impact strengths of 160 inch-pounds, 20° and 60° gloss values of 5 and 19, respectively, and a pencil hardness of 2H. The coated panels passed a 0.125 inch conical mandrel test and had a cross-hatch adhesion test value of 100% pass.

EXAMPLE 3

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

598.4 g	Polyester of Reference Example 1;
897.7 g	Hydroxyl acrylic polymer SCJ-587
466.9 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had front and back impact strengths of 120 and 40 inch-pounds, respectively, 20° and 60° gloss values of 5 and 14, respectively, and a pencil hardness of 3H. The coated panels had a 0.125 inch conical mandrel test pass rate of 95% and had a cross-hatch adhesion test value of 100% pass.

EXAMPLE 4

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

936.5 g	Polyester of Reference Example 1;
623.7 g	Hydroxyl acrylic polymer SCJ-587
382.8 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had both front and back impact strengths of 160 inch-pounds, 20° and 60° gloss

values of 4 and 10, respectively, and a pencil hardness of 2H. The coated panels passed a 0.125 inch conical mandrel test and had a cross-hatch adhesion test value of 100% pass.

EXAMPLE 5

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

454.6 g	Polyester of Reference Example 2;
314.8 g	Hydroxyl acrylic polymer SCJ-800B
202.1 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had both front and back impact strengths of 160 inch-pounds, 20° and 60° gloss values of 3 and 16, respectively, and a pencil hardness of 2H. The coated panels passed a 0.125 inch conical mandrel test and had a cross-hatch adhesion test value of 100% pass.

EXAMPLE 6

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

454.6 g	Polyester of Reference Example 2;
264.2 g	Hydroxyl acrylic polymer SCJ-587
252.6 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and

971.5 g Titanium dioxide.

The coatings on the panels had front and back impact strengths of 120 and 40 inch-pounds, respectively, 20° and 60° gloss values of 2 and 7 respectively, and a pencil hardness of 2H. The coated panels passed a 0.125 inch conical mandrel test and had a cross-hatch adhesion test value of 100% pass.

COMPARATIVE EXAMPLE 1

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

1632.1 g	Hydroxyl acrylic polymer SCJ-800B
310.9 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had front and back impact strengths of less than 20 and 20 inch-pounds, respectively, 20° and 60° gloss values of 59 and 98, respectively, and a pencil hardness of 5H. None of the coated panels passed a 0.125 inch conical mandrel test and none passed the cross-hatch adhesion test.

COMPARATIVE EXAMPLE 2

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

1379.5 g	Hydroxyl acrylic polymer SCJ-587
563.5 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;

23.3 g Modaflow flow control agent; and
971.5 g Titanium dioxide.

The coatings on the panels had both front and back impact strengths of less than 20 inch-pounds, 20° and 60° gloss values of 35 and 90, respectively, and a pencil hardness of 5H. None of the coated panels passed a 0.125 inch conical mandrel test and none passed the cross-hatch adhesion test.

COMPARATIVE EXAMPLE 3

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1. The amorphous hydroxyl polyester used in this example is a commercially-available polyester supplied by Ruco Polymer Corporation as Rucote 107 and has an ICI melt viscosity of 40, a hydroxyl number of 47 and a Tg of 58°C.

311.0 g Amorphous polyester (Rucote 107);
478.2 g Hydroxyl acrylic polymer SCJ-800B;
182.7 g Caprolactum-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g Dibutyltin dilaurate;
19.4 g Benzoin;
23.3 g Modaflow flow control agent; and
971.5 g Titanium dioxide.

The coatings on the panels had front and back impact strengths of 100 and <20 inch-pounds, respectively, 20° and 60° gloss values of 5 and 30 respectively, and a pencil hardness of 4H. The coated panels had a 0.125 inch conical mandrel test pass value of 90% and had a cross-hatch adhesion test value of 100% pass.

COMPARATIVE EXAMPLE 4

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

965.7 g	Amorphous polyester (Rucote 107);
643.1 g	Hydroxyl acrylic polymer SCJ-800B;
334.2 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had front and back impact strengths of 20 and <20 inch-pounds, respectively, 20° and 60° gloss values of 34 and 80 respectively, and a pencil hardness of 3H. The coated panels has a 0.125 inch conical mandrel test pass value of 25% and had a cross-hatch adhesion test value of 100% pass.

COMPARATIVE EXAMPLE 5

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

311.0 g	Amorphous polyester (Rucote 107);
396.6 g	Hydroxyl acrylic polymer SCJ-587;
264.4 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had front and back impact strengths of 60 and <20 inch-pounds, respectively, 20° and 60° gloss values of 7 and 44

respectively, and a pencil hardness of 5H. The coated panels had a 0.125 inch conical mandrel test pass value of 50% and had a cross-hatch adhesion test value of 100% pass.

COMPARATIVE EXAMPLE 6

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

901.6 g	Amorphous polyester (Rucote 107);
600.4 g	Hydroxyl acrylic polymer SCJ-587;
441.1 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had front and back impact strengths of 40 and 20 inch-pounds, respectively, 20° and 60° gloss values of 14 and 54 respectively, and a pencil hardness of 4H. None of the coated panels passed the 0.125 inch conical mandrel and had a cross-hatch adhesion test value of 100% pass.

COMPARATIVE EXAMPLE 7

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

1593.3 g	Amorphous polyester (Rucote 107);
349.7 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
38.9 g	Dibutyltin dilaurate;
19.4 g	Benzoin;
23.3 g	Modaflow flow control agent; and
971.5 g	Titanium dioxide.

The coatings on the panels had both front and back impact strengths of 160 inch-pounds, 20° and 60° gloss values of 86 and 95 respectively, and a pencil hardness of 2H. The coated panels had a 0.125 inch conical mandrel test pass value of 100% and had a cross-hatch adhesion test value of 100% pass.

COMPARATIVE EXAMPLE 8

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

332.0 g	Polyester of Reference Example 1;
68.0 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
4.0 g	Dibutyltin dilaurate;
2.0 g	Benzoin;
4.0 g	Modaflow flow control agent; and
160.0 g	Titanium dioxide.

The coatings on the panels had both front and back impact strengths of 160 inch-pounds, 20° and 60° gloss values of 64 and 89 respectively, and a pencil hardness of F. The coated panels passed a 0.125 inch conical mandrel test and had a cross-hatch adhesion test value of 100% pass.

COMPARATIVE EXAMPLE 9

A powder coating composition was formulated from the materials set forth below, compounded and evaluated as described in Example 1.

132.8 g	Polyester of Reference Example 1;
196.8 g	Amorphous polyester (Rucote 107);
70.4 g	Caprolactam-blocked isophorone polyisocyanate (Hüls B-1530);
4.0 g	Dibutyltin dilaurate;
2.0 g	Benzoin;

4.0 g Modaflow flow control agent; and
160.0 g Titanium dioxide.

The coatings on the panels had both front and back impact strengths of 160 inch-pounds, 20° and 60° gloss values of 71 and 91 respectively, and a pencil hardness of H. The coated panels passed a 0.125 inch conical mandrel test and had a cross-hatch adhesion test value of 100% pass.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications will be effected within the spirit and scope of the invention.

CLAIMS

We claim:

1. A coating composition characterized by producing on shaped metal articles coatings which exhibit an ASTM D-523-85 60° gloss value of not greater than 35, an ASTM D2794-84 front/back impact strength values of at least 40/20 inch-pounds and an ASTM D-3359-83 cross-hatch adhesion pass percent value of at least 90 comprising an intimate blend in the form of a powder having an average particle size of about 10 to 300 microns of:

(1) a blend of polymers consisting essentially of:

 (A) 30 to 70 weight percent, based on the weight of the blend of polymers, of a semi-crystalline polyester having a glass transition temperature of less than 50°C, a hydroxyl number of about 20 to 100, an inherent viscosity of about 0.1 to 0.5, a melting range of about 70 to 150°C, a number average molecular weight of about 1500 to 10,000, and a heat of fusion (second heating cycle of DSC) of greater than about 5 cal/g-°C; and

 (B) 70 to 30 weight percent of a hydroxyl acrylic polymer having a glass transition temperature of greater than 40°C and a hydroxyl number of about 20 to 100; and

(2) a cross-linking effective amount of a blocked polyisocyanate compound.

2. A thermosetting coating composition according to Claim 1 wherein the semi-crystalline polyester has a Tg of less than 30°C, a melting point of 90 to 140°C, a hydroxyl number of about 30 to 80, an inherent viscosity

of about 0.1 to 0.5, a number average molecular weight of about 2000 to 6000 and a heat of fusion (second heating cycle of differential scanning calorimetry) greater than 8 cal/g-°C.

3. A thermosetting coating composition according to Claim 2 wherein the blocked polyisocyanate compound is an ε-caprolactam-blocked isophorone diisocyanate compound or an ε-caprolactam-blocked 2,4-toluene diisocyanate compound.

4. A thermosetting coating composition according to Claim 2 wherein the blocked polyisocyanate compound is an adduct of the 1,3-diazetidine-2,4-dione dimer of isophorone diisocyanate and a diol having the structure

$$OCN-R^1\left[X-R^1-NH-\overset{O}{\overset{\|}{C}}-O-R^2-O-\overset{O}{\overset{\|}{C}}-NH-R^1\right]_n X-R^1-NCO$$

wherein

R^1 is a divalent 1-methylene-1,3,3-trimethyl-5-cyclohexyl radical;

R^2 is a divalent aliphatic, cycloaliphatic, araliphatic or aromatic residue of a diol; and

X is a 1,3-diazetidine-2,4-dionediyl radical; wherein the ratio of NCO to OH groups in the formation of the adduct is about 1:0.5 to 1:0.9, the mole ratio of diazetidinedione to diol is from 2:1 to 6:5, the content of free isocyanate groups in the adduct is not greater than 8 weight percent and the adduct has a molecular weight of about 500 to 4000 and a melting point of about 70 to 130°C.

5. A coating composition characterized by producing on shaped metal articles coatings which exhibit an ASTM D-523-85 60° gloss value of not greater than 30, ASTM D2794-84 front/back impact strength values of at least 160/160 and an ASTM D-3359-83 cross-hatch adhesion pass percent value of at least 90 comprising an intimate blend in the form of a powder having an average particle size of about 15 to 75 microns of:

(1) a blend of polymers consisting essentially of:

(A) 30 to 70 weight percent, based on the weight of the blend of polymers, of a semi-crystalline polyester having a Tg of less than 30°C, a melting point of 90 to 140°C, a hydroxyl number of about 30 to 80, an inherent viscosity of about 0.1 to 0.5, a number average molecular weight of about 2000 to 6000 and a heat of fusion (second heating cycle of differential scanning calorimetry) greater than 8 cal/g-°C;

(B) 70 to 30 weight percent of a hydroxyl acrylic polymer having a glass transition temperature of greater than 40°C and a hydroxyl number of about 20 to 100; and

(2) about 5 to 30 weight percent, based on the total weight of (1) and (2), of a blocked polyisocyanate compound.

6. A coating composition according to Claim 5 comprised of:

(1) a blend of polymers consisting essentially of:

(A) 40 to 60 weight percent, based on the weight of the blend of polymers, of a semi-crystalline polyest r having a Tg of less than

30°C, a melting point of 90 to 140°C, a hydroxyl number of about 30 to 80, an inherent viscosity of about 0.1 to 0.5, a number average molecular weight of about 2000 to 6000 and a heat of fusion (second heating cycle of differential scanning calorimetry) greater than 8 cal/g-°C;

(B) 60 to 40 weight percent of a hydroxyl acrylic polymer having a glass transition temperature (Tg) of greater than 40°C and a hydroxyl number of about 20 to 100; and

(2) about 10 to 25 weight percent, based on the total weight of (1) and (2), of a blocked polyisocyanate compound.

7. A coating composition according to Claim 6 wherein the blocked polyisocyanate compound is a caprolactam-blocked polyisocyanate compound and wherein the composition contains a cross-linking catalyst.

8. A coating composition according to Claim 6 wherein the blocked polyisocyanate compound is an adduct of the 1,3-diazetidine-2,4-dione dimer of isophorone diisocyanate and a diol having the structure

$$\mathrm{OCN{-}R^1}\left[\mathrm{X{-}R^1{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R^2{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}R^1}\right]_n\mathrm{X{-}R^1{-}NCO}$$

wherein

R^1 is a divalent 1-methylene-1,3,3-trimethyl-5-cyclohexyl radical;

R^2 is a divalent aliphatic residue of a diol; and

X is a 1,3-diazetidine-2,4-dionediyl radical; wherein the ratio of NCO to OH groups in the formation of the adduct is about 1:0.6 to 1:0.8, the mole ratio of diazetidinedione to diol is from 2:1 to 6:5, the content of free isocyanate groups in the adduct is not greater than 8 weight percent and the adduct has a molecular weight of about 1450 to 2800 and a melting point of about 85 to 120°C and wherein the composition contains a cross-linking catalyst.

9. A coating composition characterized by producing on shaped metal articles coatings which exhibit an ASTM D-523-85 60° gloss value of not greater than 20, ASTM D2794-84 front/back impact strength values of at least 160/160 inch-pounds and an ASTM D-3359-83 cross-hatch adhesion pass percent value of at least 90 comprising an intimate blend in the form of a powder having an average particle size of about 15 to 75 microns of:

(1) a blend of polymers consisting essentially of:

(A) 30 to 70 weight percent, based on the weight of the blend of polymers, of a semi-crystalline polyester having a Tg of less than 30°C, a melting point of 90 to 140°C, a hydroxyl number of about 30 to 80, an inherent viscosity of about 0.1 to 0.5, a number average molecular weight of about 2000 to 6000 and a heat of fusion (second heating cycle of differential scanning calorimetry) greater than 8 cal/g-°C and comprised of:

(i) diacid residues consisting essentially of about 85 to 95 mole percent terephthalic acid residues and about 5 to 15 mole

percent 1,4-cyclohexanedicarboxylic acid residues; and

(ii) diol residues consisting essentially of residues having the formula $-O-(CH_2)_n-O-$ wherein n is 6 to 12;

(B) 70 to 30 weight percent of a hydroxyl acrylic polymer having a glass transition temperature (Tg) of greater than 40°C, a hydroxyl number of about 20 to 100;

(2) about 10 to 25 weight percent, based on the total weight of (1) and (2), of a blocked polyisocyanate compound;

(3) an acrylic polymer flow aid; and

(4) a cross-linking catalyst selected from organo-tin compounds.

10. A coating composition according to Claim 9 wherein the semi-crystalline polyester component is comprised of diacid residues consisting of about 85 to 95 mole percent terephthalic acid residues and about 5 to 15 mole percent 1,4-cyclohexanedicarboxylic acid residues and diol residues consisting of 1,6-hexanediol residues.

11. A shaped metal article coated with the reaction product of a composition comprising:

(1) a blend of polymers consisting essentially of:

(A) 30 to 70 weight percent, based on the weight of the blend of polymers, of a semi-crystalline polyester having a glass transition temperature of less than 50°C, a hydroxyl number of about 20 to 100, an inherent viscosity of about 0.1 to 0.5, a melting range of about 70 to 150°C, a number

average molecular weight of about 1500 to 10,000, and a heat of fusion (second heating cycle of DSC) of greater than about 5 cal/g-°C; and

(B) 70 to 30 weight percent of a hydroxyl acrylic polymer having a glass transition temperature of greater than 40°C and a hydroxyl number of about 20 to 100; and

(2) a cross-linking effective amount of a blocked polyisocyanate compound; said coated article exhibiting an ASTM D-523-85 60° gloss value of not greater than 35, an ASTM D2794-84 front/back impact strength values of at least 40/20 inch-pounds and an ASTM D-3359-83 cross-hatch adhesion pass percent value of at least 90.

12. An article according to Claim 11 coated with the reaction product of a composition comprising:

(1) a blend of polymers consisting essentially of:

(A) 40 to 60 weight percent, based on the weight of the blend of polymers, of a semi-crystalline polyester having a Tg of less than 30°C, a melting point of 90 to 140°C, a hydroxyl number of about 30 to 80, an inherent viscosity of about 0.1 to 0.5, a number average molecular weight of about 2000 to 6000 and a heat of fusion (second heating cycle of differential scanning calorimetry) greater than 8 cal/g-°C;

(B) 60 to 40 weight percent of a hydroxyl acrylic polymer having a glass transition temperature (Tg) of greater than 40°C and a hydroxyl number of about 20 to 100; and

(2) about 10 to 25 weight percent, based on the total weight of (1) and (2), of a blocked polyisocyanate compound; said coated article exhibiting an ASTM D-523-85 60° gloss value of not greater than 30, an ASTM D2794-84 front/back impact strength values of at least 160/160 and an ASTM D-3359-83 cross-hatch adhesion pass percent value of 100

TERNATIONAL SEARCH REP

International Application No PCT/US 91/05033

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 09 D 5/03, 175/06

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 09 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X Y	US, A, 4824909 (MASAHIKO TOGO ET AL.) 25 April 1989, see the whole document --	1-3,5-7, 9-12 1-8
X Y	US, A, 3993849 (CLAUS VICTORIUS) 23 November 1976, see col. 5, lines 26-44, abstract, claim 1 --	1-3,5-7, 9-12 1-8
Y	US, A, 4413079 (JOSEF DISTELDORF ET AL.) 1 November 1983, see col. 5, lines 30-60, abstract --	1-8

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29th October 1991	08.11.91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Danielle van der Haas

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4859760 (FRED W. LIGHT, JR. ET AL.) 22 August 1989, see column 2 - column 4; abstract; claims 1-3	1-12
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A	US, A, 4150211 (HANNS P. MüLLER ET AL.) 17 April 1979, see col. 5, lines 64-68, example 6, claim 1	1-12
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 91/05033

SA 49881

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 27/09/91
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For more details about this annex : see Official Journal of the European patent Office, No. 12/82